

CREATING FUELS IS OF POOR QUALITY

2-1

RESEARCH ON AVIATION FUEL INSTABILITY

Charles E. Baker, David A. Bittker, Stephen M. Cohen, and Gary T. Seng
National Aeronautics and Space Administration
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135 U.S.A.

SUMMARY

Current aircraft turbine fuels do not present a significant problem with fuel thermal stability. However, turbine fuels with broadened properties or nonpetroleum-derived fuels may have reduced thermal stability because of their higher content of olefins, heteroatoms, and trace metals. Moreover, advanced turbine engines will increase the thermal stress on fuels because of their higher pressure ratios and combustion temperature.

In recognition of the importance of this problem, NASA Lewis is currently engaged in a broadly-based research effort to better understand the underlying causes of fuel thermal degradation. The progress and status of our various activities in this area will be discussed in this paper. Topics to be covered include: nature of fuel instability and its temperature dependence, methods of measuring the instability, chemical mechanisms involved in deposit formation, and instrumental methods for characterizing fuel deposits. Finally, some preliminary thoughts on design approaches for minimizing the effects of lowered thermal stability will be briefly discussed.

INTRODUCTION

The purpose of this report is to define the problems associated with aircraft fuel instability, review what is currently known about the problem, describe the research program sponsored by NASA Lewis, and identify those areas where more research is needed. The term fuel instability generally refers to the gums, sediments, or deposits which can form as a result of a set of complex chemical reactions when a fuel is stored for a long period at ambient conditions or when the fuel is thermally stressed inside the fuel system of an aircraft.

Thermal instability was first identified as a problem in aviation turbine engines in the 1950's. During the 1960's, early studies in the United States on the supersonic transport (SST) gave considerable attention to the problem of fuel instability, because in this SST, the fuel was to be used as a heat sink for the wing surfaces which are heated aerodynamically. It is generally acknowledged that current aircraft turbine fuels do not present a significant problem with regard to fuel instability for current subsonic aircraft. However, turbine fuels with broadened properties or nonpetroleum-derived fuels (from shale, tar-sands, coal, etc.) may have reduced thermal stability because of their higher content of olefins, heteroatoms, and trace metals. (Heteroatoms include nitrogen, oxygen, and sulfur atoms contained in organic compounds.) Moreover, advanced turbine engines may increase the thermal stress on fuels because of their higher pressure ratios and combustion temperatures. Deposition of solids within the fuel systems of aircraft may lead to fouled heat exchangers, plugged fuel nozzles, and/or jammed fuel valves which may result in excessive oil temperatures and non-uniform fuel spray patterns which could cause distorted turbine inlet temperatures (hot spots).

During the past several years NASA Lewis has been engaged in a research and technology program to determine the effects of broadened-property fuels on engine and fuel system components and to evolve the technology needed to use these fuels. Broadening fuel properties may offer the potential for increasing the refinery yield of jet fuel. Moreover, additional energy intensive treatment of poorer quality crudes and syncrudes will be required if jet fuel with current properties is to be produced. One of the major problem areas that must be addressed is fuel instability because of the reasons given in the previous paragraph. In recognition of its importance, NASA Lewis has established a broadly-based research program to better understand the underlying causes of fuel thermal degradation. Our in-house research is supported by grants with universities and contracts with industry. The progress, status, and results for these various activities will be reviewed and discussed in the report, along with some preliminary thoughts on design approaches required to minimize the effects of lowered thermal stability. In order to place the NASA Lewis program on fuel instability in its proper perspective, we should point out that similar research programs are currently being sponsored by other U.S. Government agencies, particularly the Department of Defense. These programs have made significant contributions toward the understanding of fuel degradation processes and effects. However, it is beyond the scope of this report to discuss these programs in any detail, and they will only be mentioned in the course of providing background for the NASA-sponsored program.

NATURE OF INSTABILITY

The complex chemical and physical processes involved in the degradation of fuels have been studied extensively. The early work was covered by Nixon in a comprehensive review published in 1962 [1]. A thorough literature survey which included reports or investigations since 1962 was recently published [2] by the Coordinating Research Council (CRC), and Peat has summarized the major aspects of fuel thermal stability in a current AGARD advisory report [3]. NASA Lewis sponsored a workshop on jet fuel thermal stability in 1978 [4]. The consensus among the workshop participants concerning what is known about the chemistry and physics of fuel thermal oxidation stability included the following points:

- The initial process is the interaction of fuel and dissolved oxygen.
- The chemistry involves primarily free radical reactions, but polymerization, addition, and condensation reactions are also important.
- Deposit formation rate depends on temperature with the process starting at approximately 100° C.
- Deposit rate is affected by fuel flow parameters (velocity and Reynolds number, residence time).

E-1710

- The amount of dissolved oxygen in the fuel is important; in general, removal of oxygen significantly improves fuel stability.
- Metals have a significant effect on deposit formation, with copper being the most deleterious metal. Both homogeneous effects (dissolved metals) and heterogeneous (surface) effects have been observed.
- Deposits can form both in the liquid and vapor phases with the presence of both phases causing the greatest amount of deposits.

Nature of Chemistry of Instability

The thermal decomposition of hydrocarbons can be approximately classified into three temperature regimes as follows:

1. Low temperature - below 300° C - decomposition by autoxidation
2. Intermediate temperature - between 300° and 500° C - decomposition by further reactions of autoxidation products and by some direct pyrolysis of the fuel molecules
3. High temperature - above 500° C - decomposition by direct pyrolysis of the fuel

The first two of these temperature regimes are operative in the fuel system of aircraft. It is desirable to understand the chemical mechanism or mechanisms involved in fuel degradation in order to facilitate coping with the problem of thermal instability. Because deposit formation is such a complex process, this can best be done by first obtaining both deposit formation and chemical kinetics information for less complicated systems, namely pure hydrocarbons and binary mixtures. This knowledge can then be applied to the more complex mixtures in practical fuels. One of the first studies of this kind was reported in 1977 by Hazlett at the Naval Research Laboratory [5]. He used a jet fuel thermal oxidation tester (JFTOT) connected to a gas chromatograph to study the thermal decomposition of pure n-dodecane in the presence of dissolved oxygen. (The JFTOT will be described in a later section of this report.) He measured dissolved O₂ consumption and formation of the stable intermediate hydroperoxide ROOH as a function of temperature. The mechanisms he proposed for the reactions occurring in the low and intermediate temperature regimes are presented in Fig. 1. Reaction 1 indicates the abstraction of a hydrogen atom from the fuel RH by a reactive molecule or free radical X to form the reactive alkyl radical R• which then reacts (reaction (2)) with O₂ to form the unstable RO₂•peroxide radical. The RO₂• reacts mainly by reaction (3) with the fuel to form the stable hydroperoxide ROOH and regenerate the alkyl radical. To a much smaller extent RO₂• undergoes unknown reactions to form ultimately the harmful solid deposit and sediment. Hazlett and other investigators have shown that the amount of deposit formation is not directly related to the rate of primary fuel oxidation at low temperatures, even though the oxidation must take place in order for any solid formation to occur. Reactions of intermediate oxidation products lead to solid formation, and these reactions are not understood at present.

At intermediate temperatures the secondary reactions involve the decomposition of ROOH (reaction (5)) to form ketones, alcohols and aldehydes (reactions (6) - (8)). In addition, direct pyrolysis of the fuel molecule, also a complicated chemical process, starts to occur as shown in reaction (9). Isomerization and decomposition of the radicals formed by pyrolysis leads to olefin formation. It is clear from the complexity of this partial mechanism for a pure hydrocarbon's decomposition that the elucidation of the degradation mechanism for a practical fuel will be a formidable task indeed.

Deposit Characteristics

The fuel deposits that form in aircraft fuel systems may occur as soft gums, as strongly adhering lacquers and varnishes, or as brittle cokes [3]. Studies of the morphologies of these deposits [6,7] indicate that they are generally an agglomeration of microspheres, although plate and rod forms have also been observed. Chemical analysis of fuel deposits has revealed these additional general characteristics: (1) The hydrogen/carbon ratio is lower in the deposits than in the original fuel, (2) oxygen concentration of the deposits is much greater than in the thermally unstressed fuel, and (3) other heteroatoms such as nitrogen and sulfur are highly concentrated in the deposits, with concentrations several orders of magnitude higher than in the fuel [3]. The high concentration of heteroatoms in the deposits relative to their concentrations in the fuel is strongly supportive of the importance of these trace organic impurities in the deposit formation process. The lower hydrogen/carbon ratio in the deposits suggests that aromatic compounds play an important role in deposit formation.

EVALUATION OF INSTABILITY

Attempts to measure the amount of deposit produced by a fuel under a given set of conditions have ranged from small-scale glass laboratory devices to full-scale fuel system simulators. These devices have been thoroughly reviewed in ref. 2, and this report will concentrate on the American Society for Testing and Materials (ASTM) test methods for evaluating fuel thermal stability and on the larger dynamic fuel stressing rigs commonly referred to as laboratory simulators.

ASTM Test Methods

The first standard specification test for fuel thermal stability was the CRC Fuel Coker Test (ASTM D-1660) which was designed to simulate the fuel manifold conditions that had led in the 1950's to the first operation problems caused by fuel instability [8]. The test device consists basically of a heated tube around which fuel flows at a rate of 4.5 liters/hr, followed by a heated 25 micron filter of sintered stainless steel. The former simulates the engine's hot fuel lines, and the latter the fuel nozzles and passages where fuel deposits and sediments could be trapped. The heated tube is maintained at 150° C and the filter at 204° C, with a system pressure of 1170 kPa (150 psig). Fuel is flowed through the system for 5 hours. A fuel is rated on the basis of color change on the heated tube and on pressure drop across the filter.

Because of some difficulties with the CRC Coker, primarily large sample size, low operating pressure, and long test duration, this device has been replaced by the JFTOT (ASTM D-3241), which is now used to determine if an aviation turbine fuel meets the current thermal stability requirement. A schematic of

ORIGINAL PAGE IS OF POOR QUALITY

2-3

the JFTOT is shown in Fig. 2. A small aluminum tube is heated electrically to the desired test temperature, and fuel from the reservoir is pumped through an annulus surrounding the tube, out through a test filter, and then back to the upper portion of the fuel reservoir. If the fuel is unstable, deposits will form on the heated tube, and any particulates formed will lead to an increase in pressure drop across the filter. The standard JFTOT procedure consists of flowing 0.18 liters/hr of an aerated fuel at 3447 kPa (500 psig) nitrogen gas pressure over the heated tube (260° C) for 2 1/2 hours. The amount of deposit on the tube can be rated either visually, on a scale of 0 (no deposit) to 4 (heavy deposit), or by using a tube deposit rater (TDR) that operates on a light reflectance principle. The visual rating is the method currently called for by ASTM D-3241, and a value of 3 or less is required to meet the current specification for thermal stability. However, the TDR is frequently used in fuels research, and its scale ranges from 0 to 50, with a value of 12 to 13 generally used as an equivalent criterion for passing the standard JFTOT test. In addition to the requirement on deposits, the Δp value across the filter must not exceed 3.3 kPa (25 torr) by the end of the 2 1/2-hour test if the fuel is to pass the test. By operating the JFTOT at temperatures other than 260° C, the temperature at which a fuel just fails either of the above tests may be determined. This is referred to as the "breakpoint temperature" and is used to compare the thermal stability of fuels.

Tests for storage stability usually involve placing the fuel in a small container and aging it at temperatures sufficient to accelerate the instability process, usually 80° to 100° C, so that measurable deposits are produced in a reasonable time. An ASTM procedure (D873) has been used to predict storage stability. Fuel was placed in an oxygen bomb for 16 hours at 100° C. However, experience showed that any fuel which passed the JFTOT test (breakpoint less than 260° C) always passed this storage test. Because of this, the specification for storage stability has been dropped [3].

Laboratory Simulators

There is a large gap between the operating conditions of a device such as a JFTOT and the conditions to which fuel is subjected in an actual aircraft fuel system. A laboratory simulator is an apparatus designed to bridge this gap. Important parameters such as inlet temperature, wall temperature, fuel flow rate, residence time, Reynolds number, pressure, etc. can be accurately controlled and are representative of actual engine conditions. A schematic of a laboratory simulator used in recent thermal stability studies at the United Technologies Research Center (UTRC) under NASA sponsorship [9] is shown in Fig. 3. Two closely fitted copper-beryllium alloy blocks formed the flow channel which had a cross-section 0.254 cm (0.10 in.) high by 2.84 cm (1.12 in.) wide. Because of the high thermal conductivity of this alloy, the wall temperature of the channel was very uniform. All surfaces were plated with nickel and then gold to minimize wall-material effects. Four specimen mounts were attached along the length of the test section. Each held a stainless-steel disc that was used to determine deposit formation rate by weighing the test disc on a microbalance before and after the experiment. Heating was accomplished by cartridge heaters in both the top and bottom plates. Pressure atomizing nozzles were used to control the flow rate and to observe any degradation in flow uniformity. Test temperatures ranged from 149° to 399° C (300° to 750° F), test pressures from 690 to 2070 kPa (100 to 300 psig), and fuel flow rates from 2.14 to 21.4 grams/sec.

A laboratory simulator of somewhat similar design has been built at NASA Lewis for in-house research and is currently being checked out. The entire test section and flow system were constructed of stainless steel to avoid any possibility of accelerated fuel degradation from copper materials. The NASA facility also has space for four test specimens for each experimental run, but it is capable of a wider range of operating conditions than the UTRC simulator. The flat specimens provided by both the NASA and UTRC simulators are significantly easier to characterize by most current analytical techniques than the tubular deposits produced by the JFTOT and Fuel Coker. Because of this advantage for a flat test specimen, NASA Lewis has modified one of its JFTOTs for use with a flat sample holder [10].

DESCRIPTION OF RESEARCH

Research on fuel instability can be classified into two general types: research designed to understand chemical mechanisms and research on the behavior of actual fuels. When the elucidation of chemical mechanisms is the main objective of the research, pure compounds or "model fuels" made up of a mixture of a few pure compounds are usually employed in order to simplify the chemistry. Compounds containing heteroatoms or trace metals are then added in small amounts to determine their effects on fuel stability. Other research efforts concentrate on the deposits produced by actual fuels when they are thermally stressed under controlled conditions. As has previously been discussed in this report, practical fuels are so complex and contain such a variety of trace impurities that mechanism studies using them would be extremely difficult. Common to both these types of research is the need to characterize the resulting fuel deposits. A variety of analytical techniques is required to provide information on both elemental and molecular composition. NASA Lewis' current work on fuel stability, both in-house and under grant or contract will be reviewed according to these three categories of research.

Chemical Mechanism Research

A modified JFTOT procedure was used in an in-house study to evaluate deposit and sediment formation for four aerated pure hydrocarbon fuels over the tube temperature range 150° to 450° C [11]. Stainless steel heated tubes rather than the usual aluminum tubes were used to permit higher test temperatures and to increase the deposition rate and thereby reduce test time. Four fuel types were studied: a normal alkane (n-decane), an alkene (1-hexene), a naphthene (cyclohexane), and an aromatic (benzene). Some results from this study are shown in Fig. 4, where tube deposit amounts, expressed as net TDR values, are plotted against tube position. TDR values are approximately proportional to deposition rate. At the lower temperatures of 150° and 250° C, all four fuels produced only small amounts of deposit during the 40 minute run, with TDR values less than 5. At 350° C the olefinic fuel, 1-hexene, formed the largest amount of deposit, cyclohexane the second largest, with the other two fuels forming much less deposit. The fact that 1-hexene formed the most deposit is consistent with its susceptibility to oxidation and polymerization. At the higher temperatures of 400° and 450° C all fuels except benzene formed large amounts of deposit, with TDR values of 40 to over 50. It is not surprising that benzene formed much less

ORIGINAL PAGE IS OF POOR QUALITY

2-4

deposit that the other three fuels. This can be attributed to the benzene aromatic structure, which is highly resistant to oxidation [12]. However, substituted benzenes and multi-ringed compounds are generally less resistant to oxidation. Sediment formation was also measured in these experiments and is shown in Fig. 4 as Δp in kilopascals (torr). For these fuels only benzene showed any significant Δp increase. Thus in these experiments, the aromatic benzene appears to form considerable sediment but very little deposit.

This research effort utilizing a modified JFTOT to thermally stress hydrocarbons is continuing. Effects of deoxygenation and pre-stressing of the fuel are currently under investigation. Liquid and gas chromatography as well as mass spectrometry will be used to determine reaction products, including chemical precursors that ultimately lead to deposits, in an effort to increase our understanding of the decomposition mechanisms involved in the fuel degradation process.

Effects of Fuel Nitrogen - We have already mentioned that heteroatoms such as nitrogen that are present in fuels seem to be concentrated in the fuel deposit. A number of experiments have been carried out in which a fuel is spiked with small amounts of nitrogen-containing compounds that are known to occur in actual fuels, in an effort to determine their effect on fuel deposit rates. Some results of this type experiment based on data from ref. 13 are shown in Fig. 5(a). Deposit rate for Jet-A and Jet-A spiked with 0.1 percent N from 2,5 dimethylpyrrole is plotted against temperature. It is clear from the figure that the deposit rate for the spiked Jet-A is dramatically higher at a given temperature, and that the increase in deposit rate with temperature is also considerably greater. In Fig. 5(b) the breakpoint temperature for Jet-A and Jet-A spiked with 0.01 to 0.1 percent nitrogen from pyrrole (a single-ringed N-containing compound) and indole (a double-ringed N-containing compound) are compared [14]. Since breakpoint depends on the rate of deposit formation, based on the results shown in Fig. 5(a), one would expect a reduced breakpoint for the spiked fuels. This is indeed what was observed. The Jet-A spiked with pyrrole and indole have breakpoint temperatures about 40° C and about 20° C less than the unspiked Jet-A, respectively.

Under a NASA grant with the Colorado School of Mines, Daniel has also studied the effect of various organic nitrogen compounds on deposit formation in both Jet-A and a simple model fuel [15]. He selected four classes of nitrogen compounds for study, each of which is found in petroleum and/or synthetic crudes: pyrroles, indoles, pyridines, and quinolines. The effect on deposition rate as a function of the amount of nitrogen added is shown in Fig. 6 for the four parent compounds. In this figure, the amount of deposit (expressed as micrograms) produced in 168 hours at 130° C is plotted against parts per million of nitrogen added to Jet-A. Pyridine and quinoline both show a large increase in deposition over unspiked Jet-A and this increase is strongly dependent on concentration. Conversely, indole and pyrrole exhibit only a small enhancement in the amount of deposit produced, and the increase is only slightly concentration dependent. Daniel pointed out that pyridine and quinoline each contain a nitrogen atom which contributes a single electron to the bonding in the ring, whereas in indole and pyrrole the nitrogen atom contains an unbonded electron pair which enters into the bonding of the ring. Based on these results, Daniel suggested that different mechanisms were operative in the two cases. The results of this figure may seem somewhat contradictory to those of Fig. 5(b) where pyrrole and indole produced a significant decrease in breakpoint temperature when used to spike Jet-A. It should be noted that the concentrations shown in Fig. 5(b) are 100 to 1000 ppm (0.01 to 0.1 percent) nitrogen versus a maximum of 30 ppm for Fig. 6. These large differences in nitrogen concentration plus the approximately 100° C difference in deposition temperature may have resulted in different mechanisms for the deposition process in the two sets of experiments. Nonetheless, because of the complexity of the degradation process and the presence of a great variety of trace impurities in fuels, seemingly contradictory results are not uncommon.

Oxidation Rates and Gum Formation - In an ongoing NASA-funded research contract with SRI-International, Mayo has been studying oxidation and deposit precursor formation in hydrocarbon fuels. His present approach involves measuring the rates of oxidation and rates of gum formation in an effort to relate fuel instability to the types of hydrocarbons and trace heteroatoms present in the fuels. He has found that the trace quantities of reactive components are depleted first and are concentrated in the resulting gums. The rate of oxidation may be either increased or decreased by these minor components. Some recent results [16] are presented in Fig. 7. Here, the oxygen absorbed by n-dodecane to which varying amounts of indene have been added is plotted against oxidation time. The amount of gum formed during each experiment is also shown. Indene is known to have a much faster oxidation rate than pure (or neat) n-dodecane. However, the figure shows that when a very small amount (0.009 molar) of the fast-oxidizing indene is added to the slow-oxidizing dodecane, the oxidation rate of dodecane is retarded rather than increased. From a simplistic point of view, one would expect the presence of indene to increase dodecane's oxidation rate. In fact, the oxidation rate for the indene-dodecane mixture does not exceed the oxidation rate of pure dodecane until the concentration of indene is increased to 1 molar. These results are consistent with results found by Russell many years ago for the cooxidation of cumene and tetralin [17]. It should be noted, however, that although the addition of 0.108 molar indene to dodecane slightly reduces the oxidation rate, the amount of gum formed is increased by more than a factor of 50. Since gums are believed to be precursors to solid deposits, these results illustrate that although oxygen plays a key role in deposit formation, the rate of oxidation does not directly correlate with the amount of deposit formed.

ESR Studies of Fuel Instability - An electron spin resonance (ESR) spectrometer responds to the presence of an unpaired electron in a chemical species. Such species are by definition free radicals, and we have already pointed out that the chemistry of fuel deposit formation involves primarily free radical reactions. Thus, an ESR spectrometer capable of operating at high temperatures and pressures can be used to directly monitor some of the important reactions occurring during deposit formation. We believe that the use of ESR to study fuel degradation offers the potential for significantly increasing our understanding of the reaction mechanisms and kinetics involved in this complex process. Accordingly, NASA Lewis has recently entered into an Interagency Agreement with the Oak Ridge National Laboratory (ORNL) to study free radical reactions in model compounds representative of constituents of jet fuel using ESR.

In previous research at ORNL involving coal liquids, Livingston and Zeldes developed a flow apparatus to use with an ESR spectrometer to study fluids at high temperatures and pressures [18]. Only minor modifications to this apparatus were required to enable work on fuel thermal stability to be undertaken. The

flow system used in conjunction with the ESR spectrometer is shown in Fig. 8. A liquid sample contained in a reservoir is purged with helium to remove dissolved oxygen. The liquid flows to a positive displacement high pressure pump, and pressures from 70 to 135 atm were used with a flow rate of 1 ml/min. There is provision for injecting a gas such as oxygen at high pressure. The liquid flows through a silica capillary that traverses the microwave cavity of the ESR spectrometer and then to a back pressure regulator where the system pressure is set. The liquid exiting the regulator is at atmospheric pressure and may be recirculated as shown in Fig. 8 or collected without recirculation for subsequent analysis. Thermal production of radicals is achieved by heating the silica capillary with air that has been heated electrically. The capillary is surrounded by a vacuum jacketed silica tube, and the air flows in the annular space. Radicals are also produced photolytically. This is done by focusing UV from a 500 W high pressure mercury arc onto the sample within the capillary. Photolysis is used at room temperature and up to temperatures where thermal production of radicals becomes fast enough to see signals. Typical steady-state concentrations of radicals from hydrocarbons are in the micromolar region with mean lifetimes ranging downwards from typical room temperature values near 1 millisecond.

A wide variety of model compounds is being examined that give observable spectra at temperatures up through the intermediate regime (through 300° C). Compounds include n-dodecane, aromatic hydrocarbons, unsaturated hydrocarbons, and spiking agents. Much of the work centers upon oxidizing effects and includes the use of peroxides and hydroperoxides as free radical initiators. The initial phase is a broadly based exploratory survey to search out major reaction pathways that will subsequently be examined in detail.

Deposit Formation in Practical Fuels

The deposit formation rate of actual fuels is usually determined in a flow device generally referred to as a laboratory simulator. Such devices are also capable of providing relatively heavy deposits on flat test specimens which are more easily analyzed and characterized than JFTOT tubes. The schematic of a laboratory simulator used by Vranos under contract to NASA Lewis was described previously in the discussion of Fig. 3. Vranos has used this apparatus to determine the thermal stability of four actual hydrocarbon fuels under conditions representing operation of an aircraft gas turbine engine [9, 19]. Surface temperature was varied from 149° to 399° C (300° to 750° F) for fuel flows of 0.64 to 12.8 grams per second (0.75 to 15 gal/hr) at pressures of 2040 kPa (300 psig). Test times varied from 1 to 8 hours. The rate of deposition was obtained by measurement of the weight gained by metal discs located along the channel wall.

Figure 9 shows representative results for the four fuels using stainless steel test discs: Jet A, home heating oil, a straight run diesel which has no cracked stock, and a normal diesel which has a large cracked fraction. Below 260° C (500° F), where there is an apparent change in mechanism, Jet A, straight run diesel, and the cracked diesel all had comparable deposition rates. Above 260° C, Jet A had the lowest rate, straight run diesel somewhat higher, and cracked diesel the highest. Up to 260° C the home heating oil had the highest rate while above 260° C it was lower than the cracked diesel.

The effect of wall material was determined by using stainless steel, aluminum, and brass test discs. Stainless steel and aluminum gave comparable results while the brass specimens gave a significant increase in deposition rate. Tests were also conducted in a static reactor at temperatures of 149° to 427° C (300° to 800° F) for times of 1. minutes to 2 hours. Much smaller deposition was found, indicating the importance of fluid transport in the deposition mechanism. As-received and stressed fuels were examined by liquid chromatography in an attempt to detect any changes in fuel composition caused by the heating. It is known that the changes being sought are very small and no differences were found, probably due to the limits of detection of the instrument.

The strong temperature dependence of deposition rate suggests that an Arrhenius plot, log of deposition rate versus reciprocal temperature, might correlate the data. Figure 10 is such a plot by Vranos [9] of his earlier data for Jet-A at two different flow rates. The overall activation energy, given by the slope of the lines, is in reasonable agreement with some previous results for Jet-A [20]. At higher flow rates, the deposit rate is lower at the same wall temperature, yet the temperature dependence, or activation energy, is approximately the same. The lower deposit rate at increased flow points out the importance of bulk-fluid heating and homogeneous reaction effects on the formation of deposits. In both cases, the magnitude of the activation energy, which is much less than that for typical homogeneous reactions, suggests a surface-catalyzed process.

Additional deposit-rate studies are planned for the NASA laboratory simulator previously described. In addition, this simulator along with the NASA JFTOT modified for flat test samples, will be used to generate deposits for detailed chemical and physical analysis.

Deposit Analysis

Due to the complex and intractable nature of the deposits, as well as the small quantities generally available for analysis, the detailed molecular structure of the deposits has remained largely unknown. Recent attempts to perform detailed characterization of the deposits have involved the use of a variety of modern analytical instrumental techniques which are listed in Table I along with a brief comment about the type of information each technique is capable of producing. Each technique has the potential to provide a portion of the structural information sought, but each has specific limitations as well. Through in-house research efforts and sponsored studies, each of the techniques listed is or will soon be employed to characterize deposits obtained from the JFTOT flat sample holder and the NASA thermal stability laboratory simulator under varied but carefully-controlled conditions. Both well-characterized commercial fuels and model fuels prepared from representative pure compounds are being used. To provide additional information, the deposit elemental composition will be determined, and studies to identify deposit precursors in the stressed fuels will be conducted. A combination of the deposit structural information provided by the techniques described, the deposit elemental analysis, the stressing conditions, the precursor studies and the fuel composition will yield the deposit formation mechanisms, an identification of the most active fuel components, and the sensitivity of the formation rates to fuel stressing conditions. These results

should ultimately lead to deposit prevention through the knowledgeable development of fuel additives, the types and levels of refinery fuel treatment required, and future fuel system designs.

DESIGN CONSIDERATIONS

We stated in the introduction that in the future, the thermal stability of fuels may be lower and the thermal stresses to which they are subjected, higher. One way to alleviate this problem is by additional processing at the refinery. Another is for the airlines to decrease the operating time between inspections or component removal and maintenance. Either of these approaches might be prohibitive in terms of increased costs to the airlines.

The most cost effective approach to utilizing fuels of reduced thermal stability in new, higher efficiency engines is to incorporate, in the design stage, components and designs tolerant to variations in this fuel property. It is beyond the scope of this report to discuss in any detail the types of design changes that might be required, but a few comments are appropriate.

In contracted analytical studies with NASA Lewis, General Electric and LockheedCalifornia have been analyzing and assessing advanced fuel system concepts. Both contractors have identified thermal stability and freezing point as the two most important fuel properties affecting fuel system performance. They both have studied advanced fuel systems capable of using a fuel with a breakpoint temperature of about 205° C, considerably below the current specification for thermal stability (breakpoint of at least 260° C). Although the final results for these two studies are not yet available, the advanced concepts under consideration include the following approaches to reducing heat load on the fuel after it leaves the fuel tank: (1) relocate valves to lower temperature environment and use low p nozzles which permit larger injector ports, (2) use variable displacement pumps instead of the current gear type to reduce pump heat rejection to the fuel, (3) reject lubricating-oil heat to the bulk of the fuel in the fuel tanks rather than to the much smaller amount of fuel metered for the combustor, and (4) improve the thermal tolerance of fuel nozzles and fuel lines exposed to high heat load by using heat shields, insulation, and/or cooling air. While concepts such as these may potentially allow the use of fuels with reduced thermal stability, none of these concepts has been verified experimentally. Some additional words of caution are in order. At a workshop held at NASA Lewis [21], it was pointed out that heat shield and insulation devices designed to reduce heat soak-back to fuel nozzles might reduce the aerodynamic efficiency of air-blast nozzles. This would adversely affect the atomization quality of the fuel spray which is already an area of concern with alternative fuels. This example indicates that we must be wary of interaction effects when changing the design of fuel systems.

CONCLUDING REMARKS

Although fuel instability is not a serious problem for current fuels and aircraft, it could well be a major problem in the future because of the possible deterioration of the quality of petroleum crudes and the use of syncrudes. The problem could be exacerbated by the increased thermal stress that will probably be encountered in advanced turbine engines. We have tried to show in this paper that the instability of aircraft fuel is an extremely complex problem, with experimental investigations yielding results that sometimes appear to be contradictory. Although a great deal of work has been done to understand the mechanisms of deposit formation, deposit composition, the role of trace impurities, and the effects of fuel instability on airframe and engine fuel systems, much work remains to be done. It is anticipated that an increased understanding of fuel instability will lead to methods for minimizing deposit formation or of ameliorating its effects on fuel systems.

There is another potential benefit from an increased understanding of the fuel degradation process which is related to fuel processing. Petroleum refineries currently do not use any specific processing treatment to control the thermal stability of jet fuel, although selective chemical additives (anti-oxidants) are frequently used to improve storage stability. The desired level of thermal stability is a by-product of the other processing the fuel must undergo in order to meet other specifications. This practice will probably not be satisfactory for alternative fuels because of reasons already stated. However, a fundamental knowledge and understanding of the fuel degradation process will probably provide value insight as to what type or types of additional processing should be undertaken to improve the thermal stability of the resulting fuel.

Although there are many facets of the fuel instability problem that need to be explored, it is the authors' opinion that additional research with the following objectives will lead to significant benefits in understanding and dealing with fuel instability:

- Establish the roles and degree of importance of fuel hydrocarbon type and trace contaminants in determining fuel instability.
- Compare rates, morphologies, and compositions of deposits produced via simulators with actual deposits produced in an engine fuel system.
- Evolve a model which will predict fuel deposition rates in an actual engine fuel system based on input from laboratory simulators.
- Establish the relationship between storage deposits and thermal deposits. Are the mechanisms the same, precursors the same?
- Determine the effectiveness of additives (anti-oxidants, free-radical scavengers, dispersants) for improving fuel stability as well as their interactions with each other and fuel components.
- Experimentally evaluate conceptual fuel system components and fuel injectors that reduce exposure to thermal stress and are more tolerant to small amounts of deposition.

ORIGINAL PAGE IS
OF POOR QUALITY

2-7

REFERENCES

1. Nixon, A. C.: Autoxidation and Antioxidants of Petroleum. Autoxidation and Antioxidants, Vol. II, W. O. Lundberg, Ed., Interscience Publishers, Inc., New York, 1962, pp. 695-856.
2. Anon., CRC Literature Survey on the Thermal Oxidation Stability of Jet Fuel. CRC Report No. 509, Apr. 1979.
3. Peat, A. E.: Fuel Thermal Stability. Propulsion and Energetics Panel, Working Group 13 on Alternative Jet Engine Fuels, Vol. 2, R. B. Whyte, Ed., AGARD-AR-181-Vol-2, July 1982, pp. 119-141.
4. Taylor, W. F.: Jet Fuel Thermal Stability. NASA TM-79231, 1979.
5. Hazlett, R. N., Hall, J. M. and Matson, M.: Reactions of Aerated n-Dodecane Liquid Flowing Over Heated Metal Tubes. Ind. Eng. Chem., Prod. Res. Dev., Vol. 16, No. 2, 1977, pp. 171-177.
6. Schirmer, R. M.: Morphology of Deposits in Aircraft Fuel Systems. REPT-5029-68R, Phillips Petroleum Co. Res. Div., Aug. 1968.
7. Schirmer, R. M.: Morphology of Deposits in Aircraft and Engine Fuel Systems. SAE Paper 700258, Apr. 1970.
8. Smith, M.: Aviation Fuels. G. T. Foulis & Co., Ltd., Cambridge, England, 1970, pp. 89-90.
9. Vranos, A., and Marteney, P. J.: Experimental Study of the Stability of Aircraft Fuels at Elevated Temperatures. (R80-954440-17, United Technologies; NASA Contract NAS3-21593.) NASA CR-165165, Dec. 1980.
10. Cohen, S. M.: Fuels Research - Fuel Thermal Stability Overview. Aircraft Research and Technology for Future Fuels, NASA CP-2146, July 1980, pp. 161-168.
11. Wong, E. L., and Bittker, D. A.: Effect of Hydrocarbon Fuel Type on Fuel Thermal Stability. NASA TM-82916, June 1982.
12. Bol'shakov, G. F., Bushueva, E. M., and Glebovskaya, E. A.: Effect of Some Naphthene-Aromatic Hydrocarbons on Solid-Phase Formation in Hydrocarbon Fuels. Khim.Tekhnol.Topl.Masel, Vol. 12, No. 4, Apr. 1967, pp. 40-43.
13. Taylor, W. F.: The Study of Hydrocarbon Fuel Vapor Deposits. Esso Research and Engineering Co., AFAPL-TR-69-77, Sept. 1969.
14. Antoine, A. C.: Effect of Some Nitrogen Compounds on Thermal Stability of Jet A. NASA TM-82908, June 1982.
15. Daniel, S. R.: Studies of the Mechanisms of Turbine Fuel Instability. NASA CR-167963, Jan. 1983.
16. Mayo, F. R., Lan, B., Cotts, D. B., Buttrill, Jr., S.E., and St. John, G. A.: Oxidation and Formation of Deposit Precursors in Hydrocarbon Fuels. SRI-2115, SRI International, NASA CR-168121, Mar. 1983.
17. Russell, G. A.: Oxidation of Unsaturated Compounds. J. Amer. Chem. Soc., Vol. 78, No. 5, Mar. 1956, pp. 1035-1044.
18. Livingston, R. and Zeldes, H.: Apparatus to Study the Electron Spin Resonance of Fluids under High Pressure Flowing at High Temperature. Rev. Sci. Instrum., Vol. 52, No. 9, Sept. 1981, pp. 1352-1357.
19. Marteney, P. J., Colket, M. B., and Vranos, A.: Experimental Study of the Thermal Stability of Hydrocarbon Fuels. (R82-955319-20, United Technologies Research Center; NASA Contract NAS3-22511.) NASA CR-168027, Dec. 1982.
20. Vranos, A., Marteney, P. J., and Knight, B. A.: Determination of Coking Rate in Jet A Fuel. Combust. Sci. Technol., Vol. 26, Aug. 1981, pp. 171-175.
21. Gerstein, M.: Fundamentals of Gas Turbine Combustion. NASA CP-2087, 1979.

ORIGINAL PAGE IS
OF POOR QUALITY

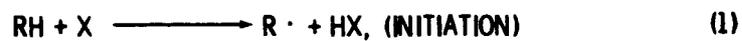
TABLE I. - MODERN INSTRUMENTATION FOR DEPOSIT CHARACTERIZATION

INSTRUMENT	INFORMATION OBTAINED
SCANNING ELECTRON MICROSCOPE (SEM)	MORPHOLOGY OF DEPOSITS THROUGH HIGH MAGNIFICATION
ENERGY DISPERSIVE ANALYSIS OF X-RAYS (EDAX)	QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF μ -SIZE SAMPLE AREAS
ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)	QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF TOP 100 Å OF SAMPLE SURFACE - PROVIDES BONDING INFORMATION
SECONDARY ION MASS SPECTROSCOPY (SIMS)	QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF 25 TO 2500 Å LAYER OF SAMPLE PER MASS SCAN
FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)	DETERMINATION OF FUNCTIONAL GROUPS - SUPERIOR SENSITIVITY TO CLASSICAL IR
RAMAN SPECTROSCOPY	DETERMINATION OF FUNCTIONAL GROUPS - COMPLEMENTS IR
PHOTOACOUSTIC SPECTROSCOPY (PAS)	CHROMOPHORE AND FUNCTIONAL GROUP DETERMINATIONS, AND THERMAL PROPERTIES CHARACTERIZATION
PYROLYSIS/GAS CHROMATOGRAPHY-MASS SPECTROMETRY	PYROLYZED FRAGMENTS FROM DEPOSIT IDENTIFIED - MOLECULAR COMPOSITION OF ORIGINAL DEPOSIT DETERMINED

ORIGINAL PAGE IS
OF POOR QUALITY

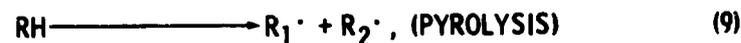
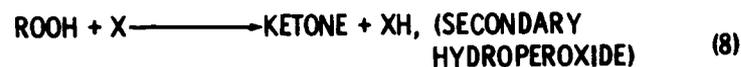
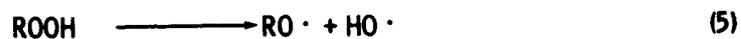
LOW TEMPERATURE

(BELOW 300° C - AUTOXIDATION)



INTERMEDIATE TEMPERATURE

(300 - 500° C)



ISOMERIZATION AND
DECOMPOSITION OF $\text{R}_1 \cdot$
AND $\text{R}_2 \cdot$ TO FORM OLEFINS

Figure 1. - Proposed mechanisms for fuel degradation.

ORIGINAL PAGE IS
OF POOR QUALITY

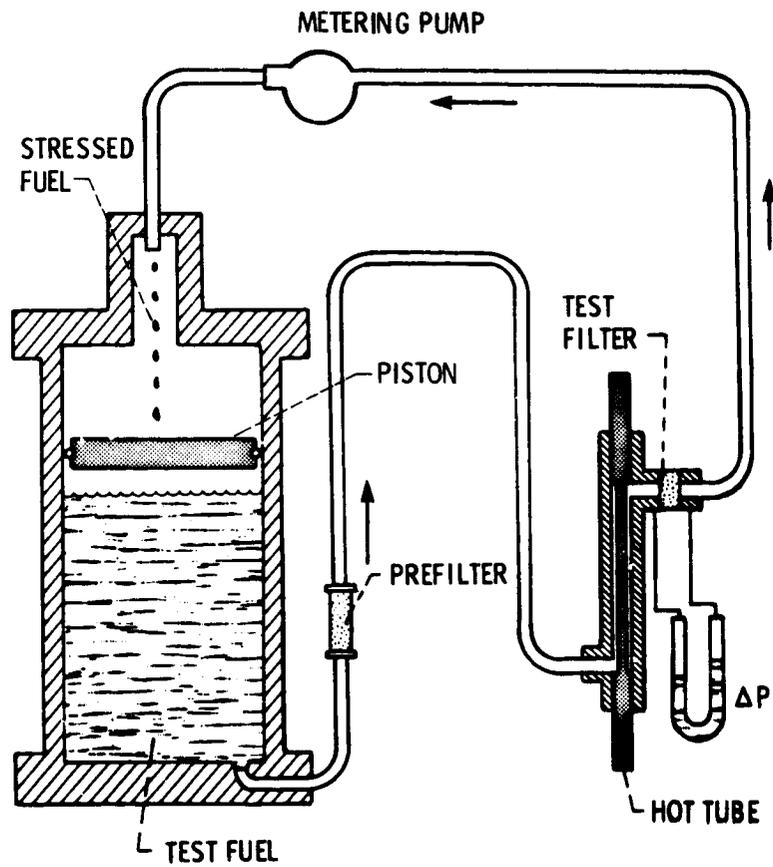


Figure 2. - Schematic of jet fuel thermal oxidation tester (JFTOT).

ORIGINAL QUALITY IS
OF POOR QUALITY

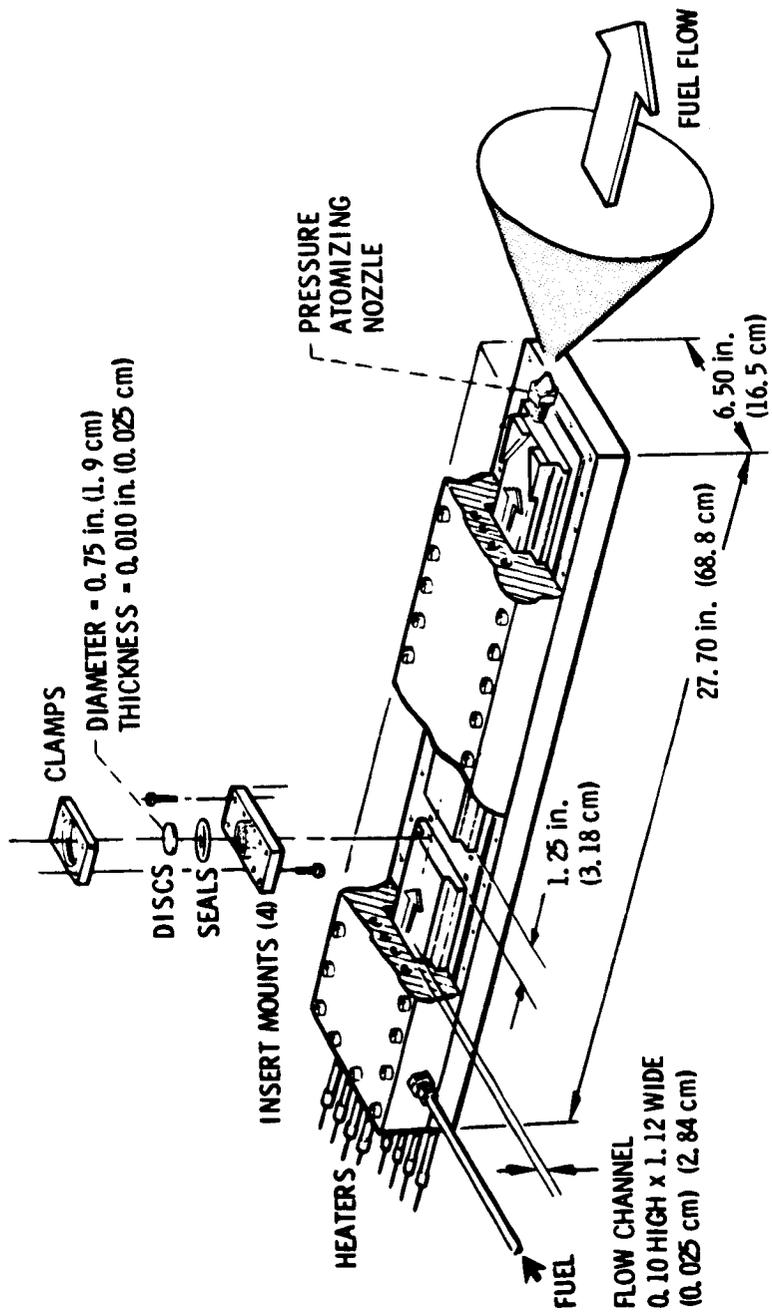


Figure 3. - UTRC thermal stability test section.

ORIGINAL PAGE IS
OF POOR QUALITY

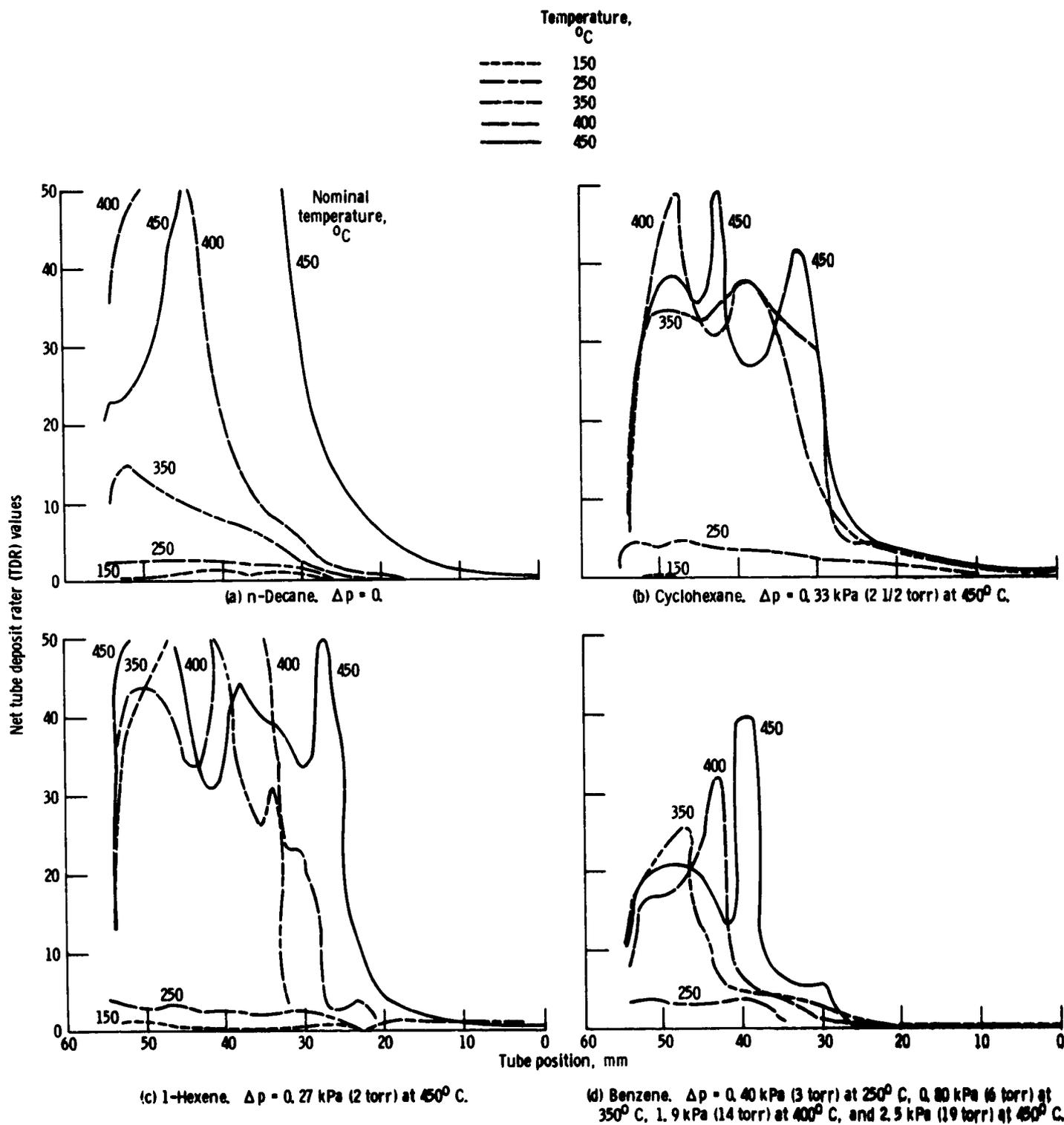
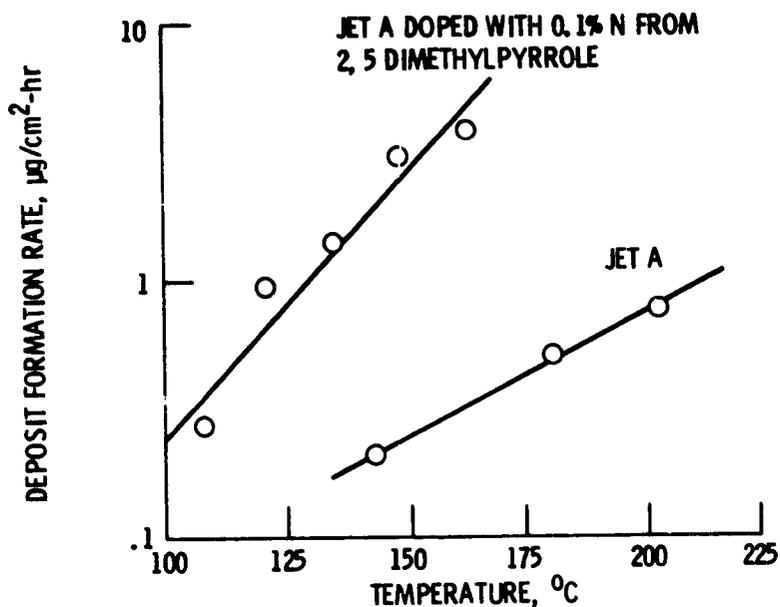
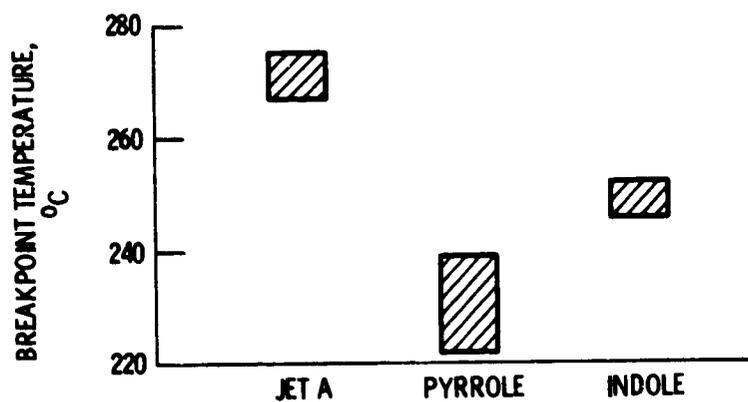


Figure 4. - Tube deposit and sediment formation for four hydrocarbon fuels.

ORIGINAL PAGE IS
OF POOR QUALITY



(a) Effect of fuel nitrogen content on deposit formation rate.



(b) Breakpoint temperatures of Jet-A and solutions of nitrogen compounds in Jet-A ranging from 0.01 to 0.1 weight percent N.

Figure 5. - Effect of fuel nitrogen content on thermal stability.

ORIGINAL PAGE IS
OF POOR QUALITY

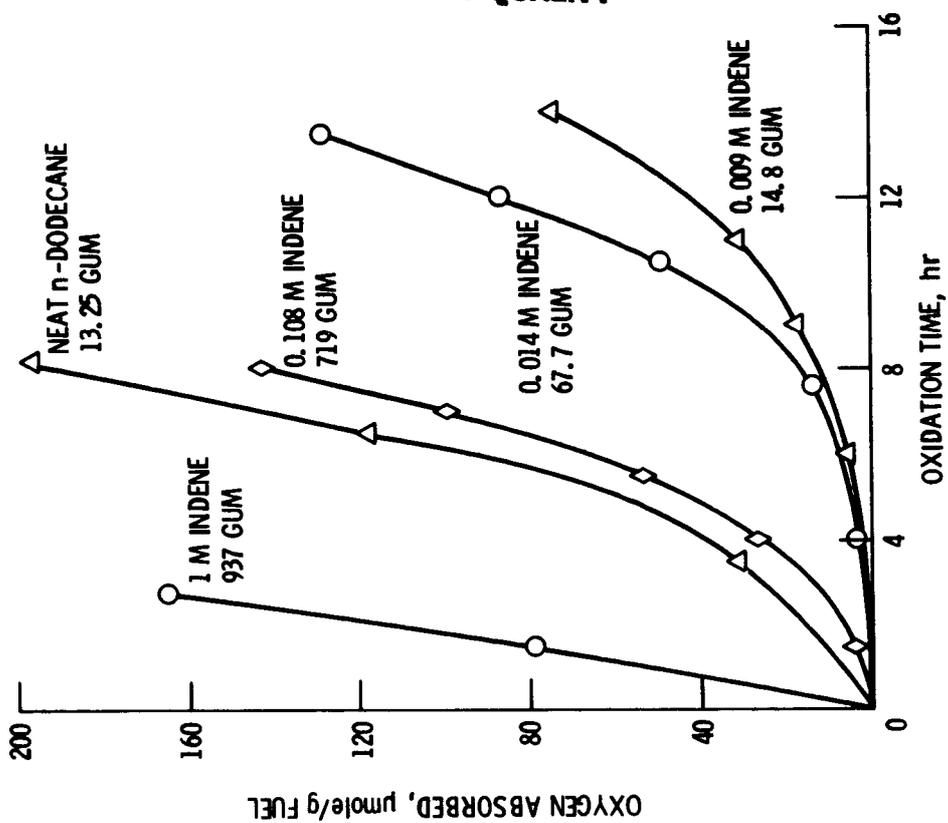


Figure 7. - Oxidations of n-dodecane with indene at 130° C
(Gum is in mg/100 g fuel, determined at 100° C).

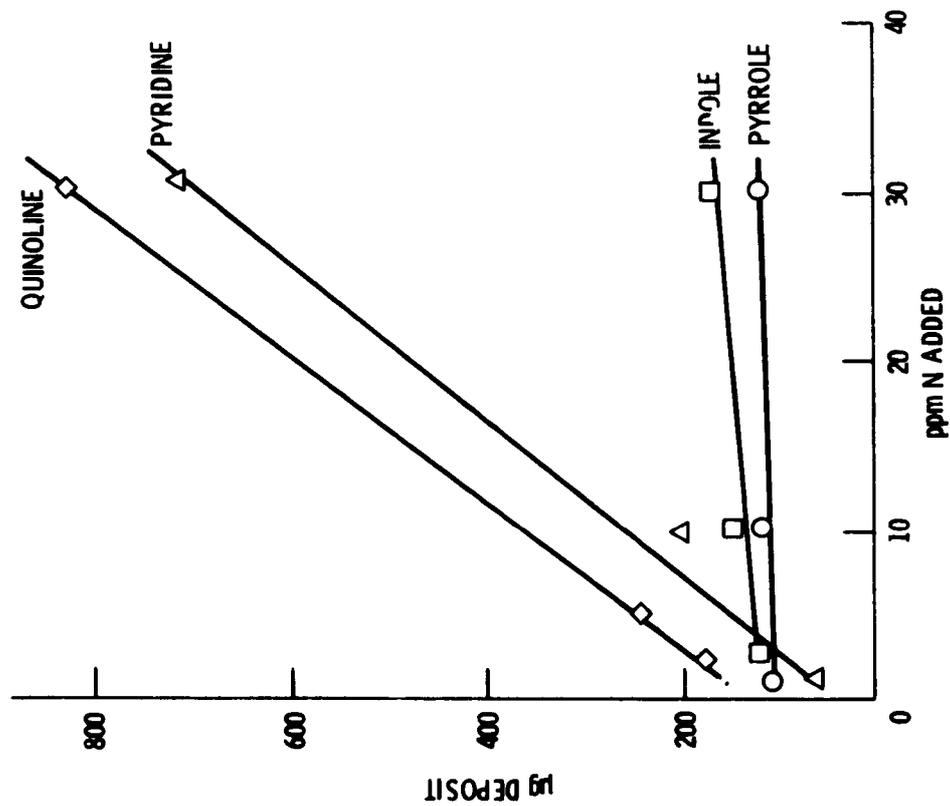


Figure 6. - Effect of added nitrogen concentration on deposit
rate at 130° C.

ORIGINAL PAGE IS
OF POOR QUALITY

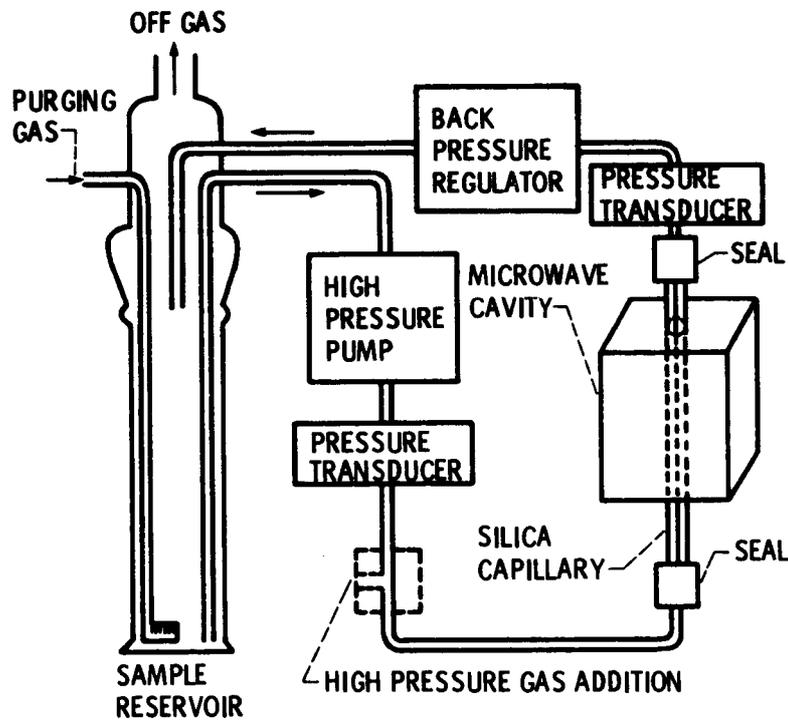


Figure 8. - Flow system for fuel thermal stability studies using electron spin resonance (ESR) spectrometer.

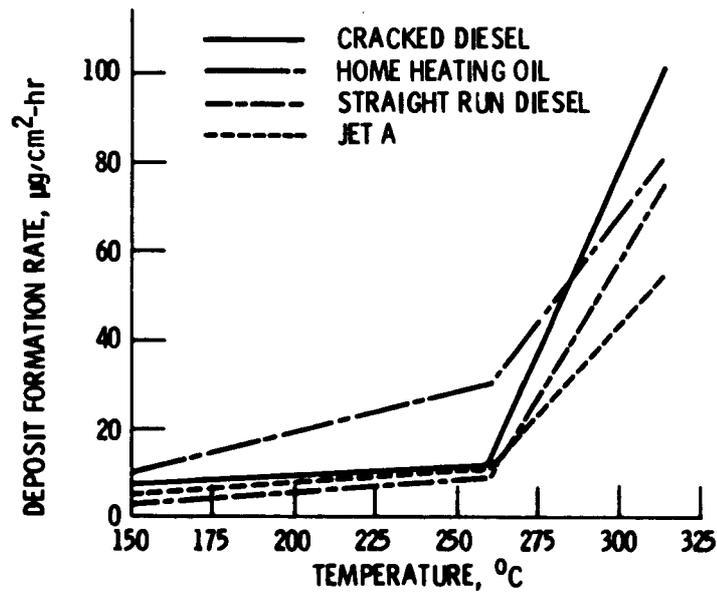


Figure 9. - Deposition rate of various fuels.

ORIGINAL PAGE IS
OF POOR QUALITY

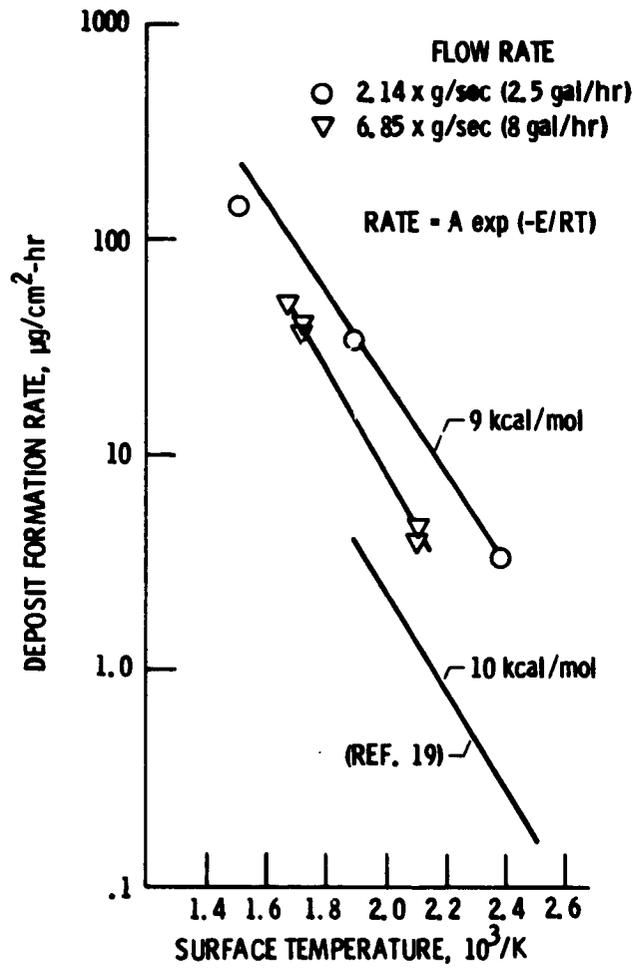


Figure 10. - Arrhenius plot of deposit rate in Jet A.

1. Report No. NASA TM-83420	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle RESEARCH ON AVIATION FUEL INSTABILITY		5. Report Date	
		6. Performing Organization Code 505-31-42	
7. Author(s) Charles E. Baker, David A. Bittker, Stephen M. Cohen, and Gary T. Seng		8. Performing Organization Report No. E-1710	
		10. Work Unit No.	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		11. Contract or Grant No.	
		13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Prepared for the AGARD Propulsion and Energetics Panel Symposium on Combustion Problems in Turbine Engines, Cesme, Turkey, October 3-7, 1983.			
16. Abstract Current aircraft turbine fuels do not present a significant problem with fuel thermal stability. However, turbine fuels with broadened properties or nonpetroleum-derived fuels may have reduced thermal stability because of their higher content of olefins, heteroatoms, and trace metals. Moreover, advanced turbine engines will increase the thermal stress on fuels because of their higher pressure ratios and combustion temperature. In recognition of the importance of this problem, NASA Lewis is currently engaged in a broadly-based research effort to better understand the underlying causes of fuel thermal degradation. The progress and status of our various activities in this area will be discussed in this paper. Topics to be covered include: nature of fuel instability and its temperature dependence, methods of measuring the instability, chemical mechanisms involved in deposit formation, and instrumental methods for characterizing fuel deposits. Finally, some preliminary thoughts on design approaches for minimizing the effects of lowered thermal stability will be briefly discussed.			
17. Key Words (Suggested by Author(s)) Fuels; Thermal stability; Oxidation; Deposit formation; Nitrogen compounds; Deposit characterization		18. Distribution Statement Unclassified - unlimited STAR Category 28	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages	22. Price*